

MATRIX-BASED FERTILIZERS: A NEW FERTILIZER FORMULATION CONCEPT TO REDUCE NUTRIENT LEACHING

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Abstract

We compared the efficacy of matrix based fertilizers (MBFs) formulated to reduce NO_3^- , NH_4^+ , and total phosphorus (TP) leaching, with Osmocoate® 14-14-14, a conventional commercial slow release fertilizer (SRF), and with an unamended control in greenhouse column studies. The MBF formulations covered a range of inorganic N and P in compounds that are relatively loosely bound (MBF1) to more moderately bound (MBF2) and more tightly bound compounds (MBF3) mixed with $\text{Al}(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ and/or $\text{Fe}_2(\text{SO}_4)_3$ and with high ionic exchange compounds starch, chitosan and lignin. When N and P are released, the chemicals containing these nutrients in the MBF temporarily bind N and P to a $\text{Al}(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ and/or $\text{Fe}_2(\text{SO}_4)_3$ starch- chitosan- lignin matrix. One milligram (8000 spores) of *Glomus intradices* was added to all formulations to attempt to enhance nutrient uptake. In this first series of experiments, soil columns were planted to white soft spring wheat (*Triticum aestivum* L.cv. Frame).

Three soils were used, a sand, a loam and a loamy sand. In several studies, SRF leachate contained higher amounts of NH_4^+ , NO_3^- and TP than leachate from all other fertilizers. Although plant biomass and yield with MBF was reduced in the first series of experiments, follow-up studies have shown that formulation adjustments allow comparable plant responses among SRF and MBFs. There were no consistent differences in the amount of NH_4^+ , NO_3^- and TP in the MBF leachates compared to the control leachate. Arbuscular mycorrhizal infection in plant roots did not consistently differ among plants growing in soil receiving SRF, MBFs and control treatments. The efficacy of MBF fertilizer strategy to reduce N and P leaching to surface has been verified and with continued work to optimize formulations this technology is expected to provide a new approach for groundwater protection, especially in easily drained soils. The approach has been submitted for patenting.

Introduction

Nitrogen (N) and phosphorus (P) are the two soil nutrients that most often limit plant growth. When N and P fertilizers are added to the soil overall N and P use efficiency is low because only the soluble fraction of these nutrients can be taken up by plants (Vassilev & Vassileva 2003). Land managers and home owners commonly apply soluble forms of N and P as inorganic fertilizers in quantities greater than plants can assimilate leading to leaching and often surface and ground water contamination (Vitousek *et al.* 1997; David & Gentry 2000; Edwards *et al.* 2000; Sharpley *et al.* 2000).

Transport of P from agricultural soils to surface waters has been linked to eutrophication in fresh water and estuaries (Bush & Austin, 2001; Broesch *et al.* 2001; Daniel *et al.* 1998). In freshwater, algal blooms contribute to a wide range of water-related problems including summer fish kills, foul odors, and unpalatable tastes in drinking water. Algal blooms cloud the water and block sunlight, causing native underwater flora to die (Zimmerman & Canuel 2000). Native underwater flora provide food, shelter and spawning and nursery habitat for aquatic fauna. When algae die and decompose, oxygen is depleted, suffocating aquatic fauna. Eutrophication accounts for about 50% of the impaired lake area and 60% of the impaired rivers in the United States. It is also the most widespread pollution problem in estuaries (Bricker *et al.* 1999).

Eutrophication is also widespread and rapidly expanding in fresh surface waters and coastal seas of the developed world. In most temperate lakes, streams and coastal ecosystems, N is the element most limiting to production of plant material such as algae, and so N inputs are the most problematic. Phosphorus is also an essential element that contributes to both freshwater and coastal eutrophication. The incidence of harmful algal blooms in lakes, streams and coastal oceans has dramatically increased in recent years (Bricker *et al.* 1999). This increase is linked to eutrophication and other factors, such as changes in aquatic food webs that may increase decomposition and nutrient recycling or reduce populations of algae-grazing fish. Increasing conversion of native lands to agriculture or development has increased the land area receiving fertilizer and contributes to N and P pollution of surface waters.

Fertilizer regimens could greatly benefit from more effective time release technologies that help managers better protect surface and ground water. We developed matrix based fertilizers (MBFs) that may reduce NH_4 , NO_3 and total P (TP) leaching. The MBFs cover a range of inorganic N and P in compounds that are relatively loosely bound (MBF1) to more moderately bound (MBF2) and more tightly bound compounds (MBF3) mixed with $\text{Al}(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ and/or $\text{Fe}_2(\text{SO}_4)_3$ and with the high ionic exchange compounds starch, chitosan and lignin. Our objective was to determine if MBFs combined with arbuscular mycorrhizae would reduce N and P leaching compared to a slow release fertilizer in sand, sandy loam and loam textured soils in a greenhouse column study.

Materials and Methods

Fertilizer Treatments

The MBF formulations in our study cover a range of common inorganic nutrient compounds combined with $\text{Al}(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ and/or $\text{Fe}_2(\text{SO}_4)_3$. Starch, chitosan and lignin were chosen because of their high concentration ionic exchange sites and their decomposition characteristics. Nutrients bound to the $\text{Al}(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ and/or $\text{Fe}_2(\text{SO}_4)_3$ starch-chitosan-lignin matrix will become increasingly available to plants as the organic components in the matrix degrade. The organic components in the matrix should degrade starch>chitosan>lignin in the order of more to less rapid. The matrix based formulations can be made to bind inorganic nutrients relatively loosely (MBF1) to more tightly (MBF3) by increasing the concentration of $\text{Al}(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ and/or $\text{Fe}_2(\text{SO}_4)_3$ and by varying the amounts of starch, chitosan and lignin in the matrix. When the matrix is applied to soil, microorganisms will degrade the starch in the matrix comparatively rapidly while chitosan will degrade less rapidly. Lignin is expected to degrade the slowest and should retain most of its ionic exchange sites for a longer time in most soil environments.

The MBF formulations are comprised of inorganic chemicals combined with starch, chitosan and lignin (Sigma, St. Louis, MO). Treatment 1 was a control; no fertilizer was applied to the columns (Fig 1). Treatment 2 was 5.0 g of the Osmocote® (14-14-14) slow release fertilizer (SRF) which was equal to 345 Φ g N and 344 Φ g P per column (Table 1). MBF1 is matrix based fertilizer formulation 1; it contains the equivalent of 152 kg N ha^{-1} and 80 kg P ha^{-1} ; MBF2 is matrix based fertilizer formulation 2; it contains the equivalent of 121 kg N ha^{-1} and 88 kg P ha^{-1} ; MBF3 is matrix based fertilizer formulation 3; it contains the equivalent of 29 kg N ha^{-1} and 143 kg P ha^{-1} . The specific composition of each formulation treatment is presented in Table 1. Osmocote® (14-14-14) has a 3-4 month nutrient release pattern at 70 EC. Treatments 3, 4 and 5 were MBF 1, MBF 2 and MBF 3 respectively. We added treatments 6, 7 and 8 to determine the effect of $Al(SO_4)_3 \cdot H_2O$ and $Fe_2(SO_4)_3$ on N and P leaching. Treatment 6 was MBF 3 +Al minus Fe which was MBF 3 with additional $Al(SO_4)_3 \cdot H_2O$. Treatment 7 was MBF 3 +Fe and minus Al, which was MBF 3 plus additional $Fe_2(SO_4)_3$. Treatment 8 was MBF 3 -Al-Fe which was MBF3 without $Al(SO_4)_3 \cdot H_2O$ or $Fe_2(SO_4)_3$. We added 8000 spores of *Glomus interadicies* in 1.00 ml of reverse osmosis water to all MBF treatments (per column) to increase plant nutrient uptake.

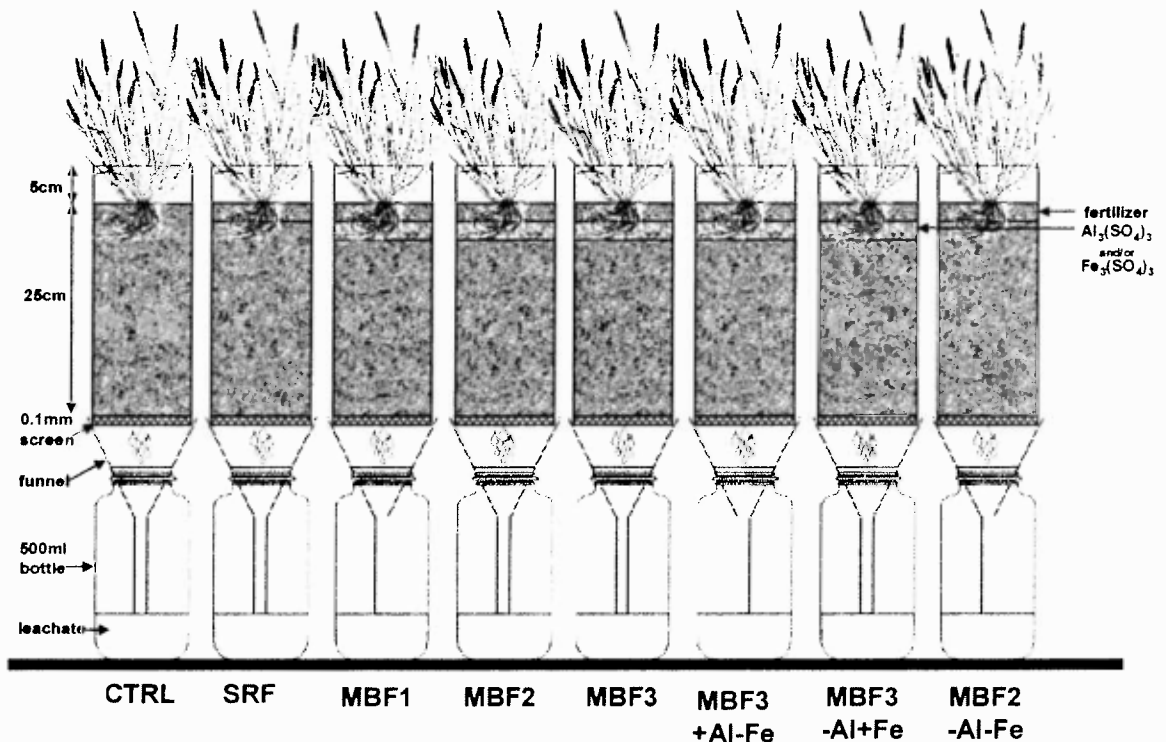


Figure 1. CTRL =control; fertilizer not applied. SRF = slow release fertilizer which received 345 :g N and 344 :g P. MBF1 = matrix based fertilizer 1 which received 313 :g N and 164 :g P. MBF2 = matrix based fertilizer 2 which received 249 :g N and 181 :g P. MBF3 = matrix based fertilizer 3 which received 60 :g N and 294 :g P. MBF3 +Al-Fe = matrix based fertilizer 3 which received 60 :g N and 294 :g P. MBF3 -Al+Fe = matrix based fertilizer 3 which received 60 :g N and 294 :g P. MBF3 -Al-Fe = matrix based fertilizer 3 which received 60 :g N and 294 :g P.

Table 1. Chemical compounds used to comprise three different matrix based fertilizers in mg N and P in each column ^a.

Treatment	1	2	3	4	5	6	7	8
Compound	CONT	SRF	MBF1	MBF2	MBF3	MBF3 +AL-Fe	MBF3 -AL+Fe	MBF3 -AL-FE
----- mg compound in each column -----								
NH ₄ NO ₃	0.000	0.210	0.000	0.000	0.000	0.000	0.000	0.000
P ₂ O ₅	0.000	0.200	0.000	0.000	0.000	0.000	0.000	0.000
K ₂ O	0.000	0.180	0.180	0.180	0.180	0.180	0.180	0.180
Ca(NO ₃) ₂ ·4H ₂ O	0.000	0.000	0.472	0.472	0.236	0.236	0.236	0.236
Al(NO ₃) ₃ ·9H ₂ O	0.000	0.000	0.750	0.750	0.000	0.000	0.000	0.000
NH ₄ (H ₂ PO ₄)	0.000	0.000	0.230	0.230	0.115	0.115	0.115	0.115
Ca(H ₂ PO ₄) ₂	0.000	0.000	0.468	0.468	0.234	0.234	0.234	0.234
Fe (P ₂ O ₇)	0.000	0.000	0.334	0.334	1.490	1.490	1.490	1.490
Al(PO ₄) ₃	0.000	0.000	0.360	0.360	0.000	0.000	0.000	0.000
Al(SO ₄) ₃ ·H ₂ O	0.000	0.000	0.488	0.366	0.000	0.488	0.000	0.000
Fe ₂ (SO ₄) ₃	0.000	0.000	0.400	0.800	1.600	0.000	1.600	0.000
Starch	0.000	0.000	1.000	1.000	1.000	1.000	1.000	1.000
Chitosan	0.000	0.000	1.000	1.000	1.000	1.000	1.000	1.000
Lignin	0.000	0.000	1.000	1.000	1.000	1.000	1.000	1.000

MBF1 is matrix based fertilizer formulation 1 = 152 kg N ha⁻¹ and 80 kg P ha⁻¹; MBF2 is matrix based fertilizer formulation 2 = 121 kg N ha⁻¹ and 88 kg P ha⁻¹; MBF3 is = matrix based fertilizer formulation 3 = 29 kg N ha⁻¹ and 143 kg P ha⁻¹. SRF = slow release fertilizer 5.0 g of Osmocote® (14-14-14) which includes NH₄NO₃, P₂O₅ and K₂O.

Table 2. Extractable nutrient concentration in a loam, sand, and loamy sand soils^a.

Soil	C	N	P	Fe	Mn	S	Si	Al	Zn
	-- g C kg ⁻¹ soil --		----- mg element kg ⁻¹ soil -----						
Loam	0.47 b	8300 a	1440 a	250 a	22 b	728 a	470 a	14 a	8.7 a
Sandy Loam	0.69 a	5900 b	861 b	120 b	35 a	462 b	329 a	5 b	7.6 a
Sand	0.28 c	6500 b	846 b	150 b	15 c	759 a	411 a	8 b	11.3 a

In each column and soil, values followed by the same letter are not significantly different as determined by the least square means test ($p \leq 0.05$, $n=3$).

Column Description

A 2.0 mm wire screen was cut into squares (125 x 125 mm) and secured to the bottom of each 10.0 cm diameter x 30 cm long polyvinyl chloride cylinder (Fig 1). A 14 cm diameter funnel was placed below each column in the rack and secured. Three kilograms of soil were placed in each column (columns were filled to 25 cm) leaving a 5 cm space at the top of each column. Soil in columns was loosely packed and then repeatedly washed with reverse osmosis water to flush nutrients that could be loosely held to soil particles. Columns were allowed to drain for 1 h prior to the start of leachate collection as described below.

Soil Descriptions

Soils having three different textures were used to determine the effectiveness of the fertilizers to reduce leaching over a range of soil types. The Brown's Creek soil was a loam and was classified as a fine, montmorillonitic, mesic Xerollic Haplargid. The Simco soil was a coarse-loamy sand and classified as a mixed non-acid, mesic Xeric Torriorthents. The Kuna soil is a sandy loam and classified as a mixed, mesic lithic Xerollic Camborthids (Collett, 1982). Soil physical and microbiological properties are presented in (Sojka et al, 2005; Entry et al, 2002). Soil chemical concentrations are presented in Table 2.

Experimental Design

The experiment was arranged in a completely randomized design (Kirk, 1982) with 8 fertilizer treatments x 3 soil textures with 3 replications. There were a total of 72 columns and 360 leachate measurements. Plants were given 100 ml reverse osmosis water each day for 70 days. Samples were measured for NH_4 , NO_3 , and TP in leachate at 7, 28, 49 and 70 days after the start of the experiment.

Fertilizer Placement and Growing Conditions

We placed the above stated amounts of $\text{Fe}_2(\text{SO}_4)_3$ and/or $\text{Al}(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ at a depth of 5 cm in columns receiving MBF treatments 6, 7 and 8. The MBF formulations were placed directly above the $\text{Fe}_2(\text{SO}_4)_3$ and/or $\text{Al}(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$. The slow release Osmocote® 14-14-14 fertilizer not receiving additional $\text{Fe}_2(\text{SO}_4)_3$ and/or $\text{Al}(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ was mixed into the top 5 cm of soil. We then placed 0.5 g of white soft spring wheat, (*Triticum aestivum* L.cv. Frame) seed on top of each column. Seeds were covered with 0.5 cm of soil. Seeds were watered with 100 ml of water daily to maintain field capacity of the soil. Leachate did not flow through columns when 100 ml water was applied. We collected leachate 7, 28, 49 and 70 days after fertilizer placement (start of the experiment) by giving plants 500 ml reverse osmosis water on the above stated days in lieu of the 100 ml daily reverse osmosis water. On each sampling day approximately 200 ml leachate was collected from each column. Subsamples were analyzed for NO_3^- and NH_4^+ and TP as described below. Throughout the experiment plants were exposed to light having a photosynthetic active radiation of 400-700 $\mu\text{mol m}^{-2} \text{S}^{-1}$ and a 14-16 h photoperiod.

Harvesting and Arbuscular Mycorrhizae Assessment

After 70 days, plants were removed from the columns and separated into roots and shoots. Roots were washed in reverse osmosis water until all visible soil particles were removed. Three g of roots were randomly selected from each plant and placed in a solution of 2.5% (w/v) KOH. The roots in the KOH solution were then placed in an autoclave for 5 min and then rinsed in 2% HCl for 24 h. Roots were then placed in 0.05 % (w/v) trypan blue in acidic glycerol for 24 hr (Koske and Gemma, 1989). Roots were observed for hyphal colonization under a 200x microscope by the cross hair intersection method (McGonigle et al., 1990). Approximately 100 intersections were scored and used to determine percent of root length

infected. Root tissue excluding roots examined for mycorrhizal infection and shoot tissue was dried at 80EC for 48 h and weighed for shoot and root biomass.

Chemical Analysis

Nitrate and NH_4^+ were determined using a Lachat Automated Ion Analyzer (Quickchem 8000 Systems, Milwaukee, WI) using the method as described by Greenberg et al., (1992). Total P in leachate was determined by digesting 25 ml aliquots in an autoclave at 103.5 kPa and 121EC for 60 min with 4.0 ml acidified ammonium persulfate (Greenberg et al., 1992). Three soil samples from each soil type were dried at 104 °C for 24 hr and passed through a 2 mm sieve. Total C was estimated by dry ashing at 525 °C and assuming C equal to 50% of loss on ignition (Nelson and Sommers, 1996). Total N was determined using standard microkjeldahl procedures modified for NO_3^- (Bremner, 1996). A 2 g sub-sample of soil was extracted with 10 ml 1 N ammonium acetate (Sims, 1989) and analyzed for Mn, Fe, Al, Si, S and Zn using inductively coupled plasma emission spectrometry (ICP).

At harvest, plant root and shoot material were dried at 65 °C for 72 hr, weighed, then ground to pass a 1 mm mesh. A 0.50 g subsample was analyzed for total N with a LECO CHN-600 nitrogen analyzer (St. Joseph, Michigan). A 0.25 g subsample was ashed at 500EC, dissolved in 25 ml of 1.0 M HCl, brought to 50 ml volume with reverse osmosis water and analyzed for P, K, Ca, Mg, Mn, Fe, Cu, B and Zn using ICP.

Statistical Analysis

All values were tested to verify normal distribution. Data were then analyzed using general linear models (GLM) procedures for a completely random design with Statistical Analysis Systems (SAS Institute Inc., 1996). In all analyses, residuals were equally distributed with constant variances. Differences reported throughout are significant at $p \leq 0.05$, as determined by the Least Squares Means test.

Results

The GLM models of leached nutrients for soil type x fertilizers x sample day, soil type x fertilizers, and soil type x sample day were not significant, therefore, statistical comparisons of NH_4^+ , NO_3^- and total P are presented for fertilizer treatments because GLM models showed these interactions were significant at $p \leq 0.05$ (Snedecor and Cochran, 1980).

We found that 45 to 58 % of the NH_4^+ , 40 to 85% of the NO_3^- and 79 to 99% of the total P was leached from the soil columns in the first 28 days after Osmocote® (14-14-14) SRF was applied (Tables 3, 4, 5; Figs. 2, 3, 4). After 70 days, SRF leachate contained a greater amount of NH_4^+ , NO_3^- and TP than leachate from all other fertilizers. In all three soils, MBFs reduced NH_4^+ in leachate by a minimum of 50%, NO_3^- leachate by a minimum of 46% and TP in leachate by a minimum of 200%. In all three soils there were no consistent differences in the amount of NH_4^+ , NO_3^- and TP in the MBF leachates than in the control leachate. Plants growing in soils receiving SRF had greater head weight, shoot, root and total biomass than all fertilizer formulations (Table 6). All fertilizer formulations and SRF plants had greater head weight, shoot, root and total biomass than plants growing in soils receiving no fertilizer (control). Arbuscular mycorrhiza infection in plant roots did not consistently differ among plants growing in soil receiving SRF and MBF formulations and plants growing in soils receiving no fertilizer (control). Plants growing in the loam soil receiving SRF treatment had greater shoot and root N concentrations than all MBF formulations except for the MBF1 shoot N concentration. Plants growing in the sand and sandy loam soils receiving SRF treatment had greater shoot N concentrations than all MBF formulations. Plants receiving SRF had

greater shoot P content than all MBF formulations. All MBF and SRF plants had greater shoot P content than plants growing in soils receiving no fertilizer (control). The concentration of K, Ca, Mg, Mn, Fe, Cu, B and Zn in root and shoot tissue did not differ ($p \leq 0.05$) among treatments (data not shown).

Discussion

We found that over 45% of the NH_4^+ , over 40% of the NO_3^- and over 79% of the total P was leached from the soil columns in the first 28 days after the Osmocote® (14-14-14) SRF was applied (Tables 3, 4, 5; Figs. 2, 3, 4). Plants receiving SRF had greater plant biomass (growth) shoot and root N and P content than all MBF formulations regardless of $\text{Al}(\text{SO}_4)_3 \text{H}_2\text{O}$ or $\text{Fe}_2(\text{SO}_4)_3$ additions. Plants receiving SRF had 15- 55% greater plant biomass than those growing in MBF formulations 70 days after application. The growth rate of plants receiving SRF was greater than those receiving MBF formulations in the 70 day time period, presumably because in soils receiving SRF the nutrients were more available to the plant. Shoot biomass, shoot N and P, and head weight were greater in plants given SRF than the MBF formulations. The MBF formulations contained nutrients bound to the $\text{Al}(\text{SO}_4)_3 \text{H}_2\text{O}$, or $\text{Fe}_2(\text{SO}_4)_3$, starch, chitosan and lignin exchange matrix and were more slowly available to plants than the SRF fertilizers. A small fraction of N and P is probably immobilized in the matrix and only available to plants over a more prolonged time period. Subsequent experiments have focused on MBF rate and formulation adjustments to produce plant growth equal to that obtained by fertilization with the SRF while still reducing N and P leaching.

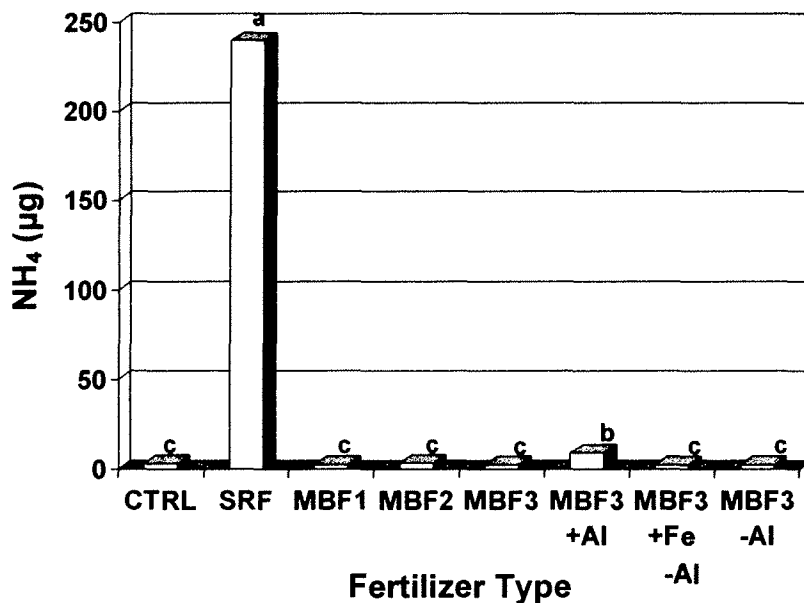


Figure 2. Total amount of NH_4 leached from soil columns growing wheat over 70 days. Bars having same letter are not significantly different as determined by the least square means test ($p \leq 0.05$), $n = 360$.

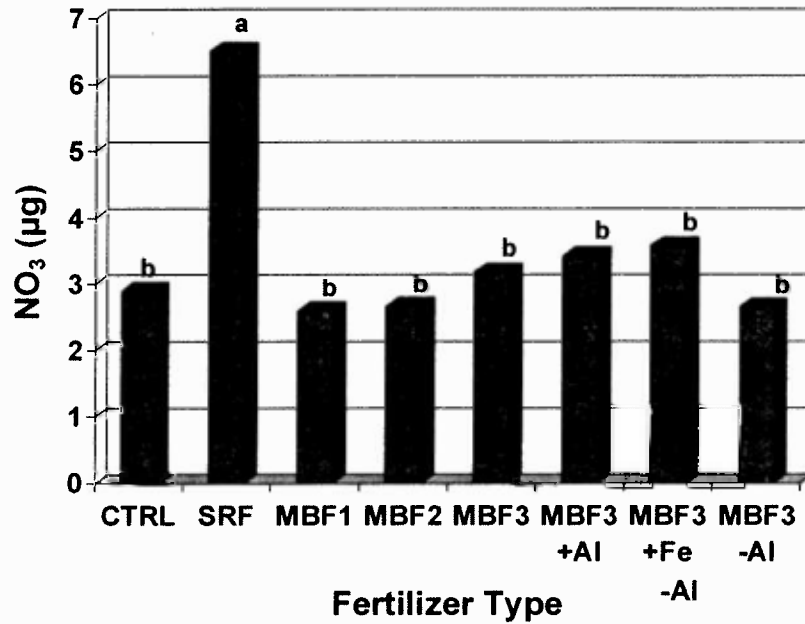


Figure 3. Total amount of NO₃ leached from soil columns growing wheat over 70 days. Bars having same letter are not significantly different as determined by the least square means test (p # 0.05), n = 360.

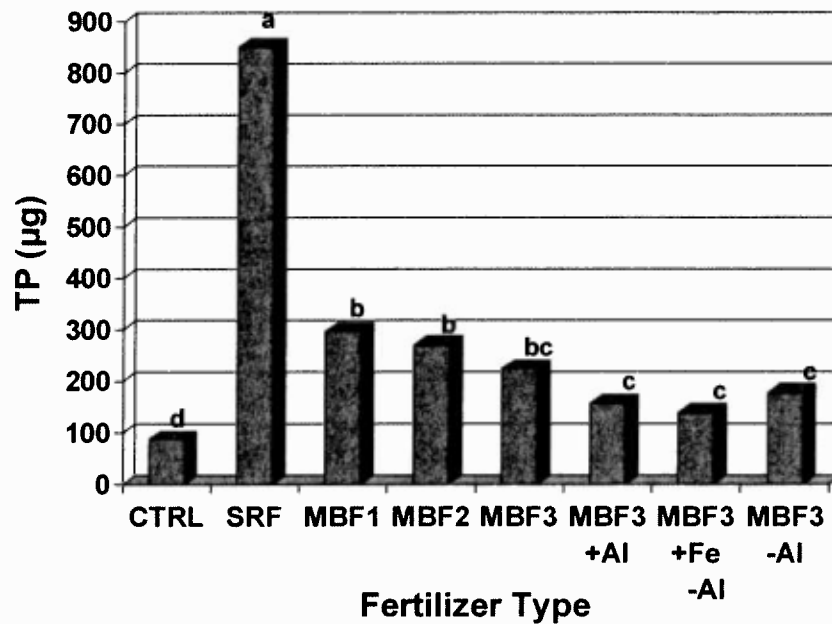


Figure 4. Total amount of total phosphorus (TP) leached from soil columns growing wheat over 70 days. Bars having same letter are not significantly different as determined by the least square means test (p # 0.05), n = 360.

Table 3. Total P NH_4^+ and NO_3^- leached from columns growing wheat in a loam soil.

Treatment	Day	mg nutrient L ⁻¹		
		Total P	NH_4^+	NO_3^-
Control (no fertilizer)	7	116.31b	3.92b	0.94b
Slow Release Fertilizer		387.03a	6.26a	1.80a
MBF 1		281.51b	1.65c	0.94bc
MBF 2		195.22a	2.55b	1.11b
MBF 3		179.92a	0.96c	0.42c
MBF 3 ! Al (SO ₄) ₃		110.04b	4.49b	0.48c
MBF 3 + Fe (SO ₄) ₃		77.17c	1.01c	0.76c
MBF 3 ! Al (SO ₄) ₃ - Fe (SO ₄) ₃		96.83bc	1.00c	1.69ab
Control (no fertilizer)	28	37.20c	1.05b	0.81b
Slow Release Fertilizer		619.84a	3.79a	1.19a
MBF 1		204.27b	0.93b	0.30b
MBF 2		68.53b	1.42ab	1.06ab
MBF 3		22.12c	1.00b	1.39a
MBF 3 ! Al (SO ₄) ₃		32.59c	1.84ab	0.63ab
MBF 3 ! Fe (SO ₄) ₃		18.02c	1.07b	0.40b
MBF 3 ! Al (SO ₄) ₃ - Fe (SO ₄) ₃		30.36c	0.89b	0.62b
Control (no fertilizer)	49	1.24b	0.73b	1.19a
Slow Release Fertilizer		22.10a	2.41a	0.71a
MBF 1		1.68b	0.45b	1.03a
MBF 2		0.67c	0.52b	0.96a
MBF 3		0.75c	0.70b	1.25a
MBF 3 ! Al (SO ₄) ₃		0.59c	1.21b	0.97a
MBF 3 + Fe (SO ₄) ₃		0.51c	0.63b	1.18a
MBF 3 ! Al (SO ₄) ₃ - Fe (SO ₄) ₃		0.82c	0.41b	1.06a
Control (no fertilizer)	70	0.37b	0.62c	0.18a
Slow Release Fertilizer		4.85a	2.84a	0.11a
MBF 1		0.48b	0.45c	0.14a
MBF 2		0.25b	0.62c	0.14a
MBF 3		0.29b	0.59c	0.14a
MBF 3 ! Al (SO ₄) ₃		0.30b	1.93c	0.19a
MBF 3+ Fe (SO ₄) ₃		0.33b	0.43c	0.18a
MBF 3 ! Al (SO ₄) ₃ - Fe (SO ₄) ₃		0.27b	0.42c	0.09a

In each column and day, values followed by the same letter are not significantly different as determined by the least square means test (($n \leq 0.05$, $n=9$).

Table 4. Total P NH_4^+ and NO_3^- leached from columns growing wheat in a sandy soil.

Treatment	Day	mg nutrient L^{-1}		
		Total P	NH_4^+	NO_3^-
Control (no fertilizer)	7	10.47c	0.49c	0.19b
Slow Release Fertilizer		160.89a	2.04b	3.91a
MBF 1		119.59b	1.42b	0.64b
MBF 2		97.92b	1.57b	0.44b
MBF 3		81.01b	0.74c	0.64b
MBF 3 ! $\text{Al}(\text{SO}_4)_3$		148.69ab	4.93a	2.82a
MBF 3 + $\text{Fe}(\text{SO}_4)_3$		94.23b	0.69c	2.03a
MBF 3 ! $\text{Al}(\text{SO}_4)_3$ - $\text{Fe}(\text{SO}_4)_3$		88.11b	1.65b	0.39b
Control (no fertilizer)	28	0.63e	0.39b	1.22a
Slow Release Fertilizer		778.84a	2.41a	0.14b
MBF 1		46.56b	0.63b	1.55a
MBF 2		15.10b	0.69b	1.33a
MBF 3		2.91d	0.77b	1.62a
MBF 3 ! $\text{Al}(\text{SO}_4)_3$		1.65d	2.02a	0.41b
MBF 3 ! $\text{Fe}(\text{SO}_4)_3$		2.05d	0.77	0.81ab
MBF 3 ! $\text{Al}(\text{SO}_4)_3$ - $\text{Fe}(\text{SO}_4)_3$		4.21d	0.63b	0.17b
Control (no fertilizer)	49	0.42b	0.37b	1.13a
Slow Release Fertilizer		3.99a	1.69a	0.96a
MBF 1		0.73b	0.42b	0.81a
MBF 2		0.49b	0.55b	0.83a
MBF 3		0.47b	0.37b	1.16a
MBF 3 ! $\text{Al}(\text{SO}_4)_3$		0.33b	1.72a	1.36a
MBF 3 + $\text{Fe}(\text{SO}_4)_3$		0.51b	0.39b	1.52a
MBF 3 ! $\text{Al}(\text{SO}_4)_3$ - $\text{Fe}(\text{SO}_4)_3$		0.50b	0.58b	1.21a
Control (no fertilizer)	70	0.45b	0.29c	0.20a
Slow Release Fertilizer		1.97a	1.46b	0.31a
MBF 1		0.46b	0.30c	0.27a
MBF 2		0.54b	0.42c	0.16a
MBF 3		0.46b	0.33c	0.18a
MBF 3 ! $\text{Al}(\text{SO}_4)_3$		0.39b	2.67a	0.32a
MBF + $\text{Fe}(\text{SO}_4)_3$		0.45b	0.35c	0.65a
MBF 3 ! $\text{Al}(\text{SO}_4)_3$ - $\text{Fe}(\text{SO}_4)_3$		0.48b	0.55c	0.18a

In each column and day, values followed by the same letter are not significantly different as determined by the least square means test ($n \# 0.05$, $n=9$).

Table 5. Total P NH_4^+ and NO_3^- leached from columns growing wheat in a sandy loam soil.

Treatment	Day	mg nutrient L ⁻¹		
		Total P	NH_4^+	NO_3^-
Control (no fertilizer)	7	93.97b	0.57b	0.61b
Slow Release Fertilizer		101.50b	6.36a	3.23a
MBF 1		117.43b	0.49b	0.67b
MBF 2		401.37a	0.54b	0.67b
MBF 3		331.37a	0.37b	0.42b
MBF 3 ! Al (SO ₄) ₃		86.40b	4.55a	0.91b
MBF 3 + Fe (SO ₄) ₃		188.96ab	0.47b	0.26b
MBF 3 ! Al (SO ₄) ₃ - Fe (SO ₄) ₃		260.78ab	0.45b	1.01b
Control (no fertilizer)	28	0.92c	0.47b	0.96a
Slow Release Fertilizer		351.18a	6.91a	1.20a
MBF 1		116.52b	0.53b	0.11b
MBF 2		31.01b	0.67b	0.33b
MBF 3		56.69b	0.68b	0.96a
MBF 3 ! Al (SO ₄) ₃		89.92ab	0.87b	1.22a
MBF 3 ! Fe (SO ₄) ₃		32.10b	0.58b	1.35a
MBF 3 ! Al (SO ₄) ₃ - Fe (SO ₄) ₃		48.71b	0.67b	0.17b
Control (no fertilizer)	49	0.48b	0.37b	1.14a
Slow Release Fertilizer		112.72a	1.19a	1.01a
MBF 1		0.86b	0.03b	1.06a
MBF 2		0.47b	0.56b	0.73a
MBF 3		1.02b	0.50b	1.01a
MBF 3 ! Al (SO ₄) ₃		0.98b	0.90ab	0.80a
MBF 3 + Fe (SO ₄) ₃		0.78b	0.42b	1.42a
MBF 3 ! Al (SO ₄) ₃ - Fe (SO ₄) ₃		0.75b	0.42b	0.49a
Control (no fertilizer)	70	0.49b	0.34b	0.18a
Slow Release Fertilizer		3.02a	0.91a	0.47a
MBF 1		0.51b	0.30a	0.25a
MBF 2		0.55b	0.50b	0.22a
MBF 3		1.02b	0.50b	1.01a
MBF 3 ! Al (SO ₄) ₃		1.45b	0.44b	0.33a
MBF + Fe (SO ₄) ₃		0.54b	0.69ab	0.17a
MBF ! Al (SO ₄) ₃		0.59b	0.34b	0.15a
MBF 3 ! Al (SO ₄) ₃ - Fe (SO ₄) ₃	0.27b	0.42b	0.96a	

In each column and day, values followed by the same letter are not significantly different as determined by the least square means test ($n \# 0.05, n=9$).

Table 6. Wheat height, biomass, and head weight after 70 days growth in a loam, sand, and loamy sand soil in greenhouse conditions^{a,b}.

Soil	Treatment	Height ---cm---	Head Weight	Shoot Biomass	Root Biomass	Plant Biomass	Mycorrhizal Infection arbuscules/mm	Shoot N	Shoot P	Root N	Root P	
												g
Loam	Control (no fertilizer)	44.0 c	6.5 c	11.5 d	12.7 c	24.2 c	3.7 b	8300 b	168.2 c	5333 b	3553 c	
	SRF	49.0 b	17.2 a	26.9 a	29.5 a	56.4 a	40.9 a	16060 a	732.6 a	7833 a	8567 a	
	MBF 1	57.9 a	12.6 b	21.8 b	24.0 b	40.0 b	20.6 a	10700 ab	278.2 b	5200 b	4123 bc	
	MBF 2	57.6 a	12.6 b	21.0 b	23.1 b	44.2 b	27.7 a	8300 b	304.6 b	4300 b	3806 bc	
	MBF 3	56.8 a	9.7 b	16.4 c	18.1 b	34.5 b	13.0 ab	7333 b	235.9 b	3933 b	4367 b	
	MBF 3 + Al-Fe	54.3 a	9.4 b	16.2 c	17.8 b	33.9 b	15.6 ab	7633 b	282.7 b	4800 b	5373 b	
	MBF 3 -Al+Fe	50.4 a	8.6 b	15.0 c	16.5 b	31.5 b	43.3 a	8467 b	221.0 b	4000 b	4123 bc	
	MBF 2, Al-Fe	55.9 a	11.7 b	19.2b c	21.1 b	34.2 b	19.6 ab	8530 b	276.6 b	4333 b	4553 b	
	Sand	Control (no fertilizer)	24.8 b	0.8 c	1.7 c	1.9 c	3.6c	16.9 a	5900 c	14.6 c	4800 b	3563 c
		SRF	51.9 a	17.3 a	28.0 a	30.9 a	58.9a	20.3 a	13733 a	614.0 a	7800 a	6073 ab
MBF 1		50.3 a	7.7 b	15.4 b	16.9 b	38.8b	8.0 ab	8666 b	134.7 b	5800 b	6226 ab	

MBF 2	51.7 a	8.9 b	15.9 b	17.5 b	33.4b	21.0 a	7566 b	197.4 b	4900 b	4280 b
MBF 3	47.6 a	6.0 b	10.1 b	12.1 b	23.1b	28.3 a	7033 b	153.7 b	4566 b	4120 bc
MBF 3 + Al-Fe	51.4 a	6.4 b	11.7 b	12.8 b	24.5b	6.1 b	7433 b	193.8 b	4200 b	5617 b
MBF 3 -Al+Fe	47.1 a	6.9 b	12.4 b	13.7 b	26.1b	5.1 b	7100 b	151.6 b	4833 b	3687 b
MBF 2-Al-Fe	52.7 a	8.6 b	16.3 b	17.9 b	34.2b	20.9 a	7666 b	180.2 b	4500 b	3390 b
Sandy Loam Control (no fertilizer)	39.5 b	2.8 c	5.9 c	6.4 c	12.4 c	26.3 a	6466 c	47.2 c	5400 b	3300 c
SRF	48.0 a	18.1 a	28.7 a	31.6 a	60.3 a	24.1 a	15833 a	586.9 a	7400 a	5806 b
MBF 1	56.9 a	10.6 b	20.0 b	22.0 b	41.9 b	35.2 a	7166 b	194.8 b	5100 b	3912 bc
MBF 2	54.0 a	10.3 b	18.4 b	20.3 b	38.7 b	15.4 a	8300 b	257.8 b	4066 b	5247 b
MBF 3	53.0 a	9.6 b	17.8 b	19.5 b	37.3 b	17.6 a	7600 b	210.7 b	4133 b	4346 b
MBF 3 + Al-Fe	52.0 a	9.1 b	16.5 b	18.1 b	34.6 b	24.3 a	9500 b	191.6 b	3900 b	5246 b
MBF 3 -Al+Fe	50.9 a	8.7 b	16.3 b	17.9 b	34.2 b	29.6 a	9833 b	161.2 b	4800 b	5183 b
MBF 2-Al-Fe	50.1 a	8.9 b	16.2 b	17.8 b	34.0 b	26.3 a	7566 b	182.5 b	4133 b	4057 b

In each column and soil, values followed by the same letter are not significantly different as determined by the least square means test (p , 0.05, $n=9$).

MBF1 is matrix based fertilizer formulation 1 = 152 kg N ha-1 and 80 kg P ha-1; MBF2 is matrix based fertilizer formulation 2 = 121 kg N ha-1 and 88 kg P ha-1; MBF3 is matrix based fertilizer formulation 3 = 29 kg N ha-1 and 143 kg P ha-1.

Direct losses of P from fertilizer leaching or runoff usually result when fertilizer application is coincident with heavy rain events (Haygarth and Jarvis, 1999). Our results suggest that current commercial slow release formulations applied at optimal rates for crop nutrition and growth are still highly susceptible to nutrient leaching. Therefore, even if agricultural and turfgrass operators were to apply nutrients in amounts anticipated to meet plant requirements over the growing season, substantial amounts of N and P could be leached. The problem is often exacerbated because some turfgrass operations and home lawns have nutrients applied at rates exceeding plant requirements (Hart et al., 2003). Several studies indicated that sediment bound P concentrations in runoff generally increase as soil P concentrations increase (Sharpley et al., 1993; Pote et al., 1999; Cox and Hendricks, 2000). Long-term overfertilization of soils contributes to eutrophication of surface waters (Sims, 1993; Frossard et al., 2000).

Conventional SRF formulations such as single super phosphate (SSP), monoammonium phosphate (MAP) and diammonium phosphate (DAP) were developed with the goal of minimizing the production costs per unit of soluble P. The study of SSP, MAP and DAP modification to reduce susceptibility to P runoff and leaching has been limited (Hart et al., 2003). Slow-release fertilizers have been employed to reduce direct fertilizer runoff losses. Nutrient leaching from slow release fertilizers is reduced through degradation of an organic or inorganic coating around a core of inorganic fertilizer. Quin et al. (2003) describe coating a DAP with a slurry of elemental sulfur which provides a short-term barrier to water. Field trials demonstrated an approximate 40% reduction of P runoff during the first runoff event after application. Nash et al. (2003) conducted laboratory dissolution studies comparing SSP and a dry sulfur-coated superphosphate, in which sulfate of ammonia was the binding agent. The authors found that the water-extractable P was greater from the coated superphosphate fertilizer treatments (6.6%) compared to 4.8% from superphosphate treatments. The rapid dissolution of the S-coated superphosphate resulted from the rapid solubilization of the sulfate of ammonia in the extraction procedure, and with it removal of the sulfur coat and protection against P dissolution in the granules (Hart et al., 2003).

Commercial slow release fertilizers can be classified into two basic groups: low solubility and polymer coated water soluble fertilizers (Blaylock et al., 2005). The polymer coated slow release fertilizers are water soluble and can exhibit consistent nutrient release rates. However average soil temperature and moisture need to be known. The fertilizers are characterized by one or more polymeric resins surrounding the fertilizer. The duration of nutrient release is controlled by the porosity of the resin coating. A more porous coating results in quicker release. When polymer coated slow release fertilizers are applied to the soil, the water in the soil enters the fertilizer granule through micropores which dissolves the nutrients. Nutrients are then steadily released through the same pores. The rate of nutrient release of polymer coated slow release fertilizers is influenced by soil temperature: the higher the soil temperature, the greater the release rate (Blaylock et al., 2005). Release rate is hypothesized to not be significantly influenced by microbiological decomposition, soil moisture, soil type or pH. However, the polymers used eventually degrade in soil (Basfar et al., 2003; Bonhomme et al., 2003; Lehmann et al., 2000; 1998) and the degradation rate influences nutrient release from the polymer.

The MBF formulations in our study cover a range of common inorganic nutrient compounds combined with $\text{Al}(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ and/or $\text{Fe}_2(\text{SO}_4)_3$ and the high ionic exchange compounds starch, chitosan and lignin. These formulations allow nutrients to bind with the $\text{Al}(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ and/or $\text{Fe}_2(\text{SO}_4)_3$ - lignin - chitosan matrix, substantially reducing leaching. Normally, the ions bound to the $\text{Al}(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ and/or $\text{Fe}_2(\text{SO}_4)_3$ - lignin - chitosan matrix gradually become

available to plants over several months or seasons. These matrix based formulations cover a range of inorganic N and P in compounds that are relatively loosely bound (MBF1) to more moderately bound (MBF2) and more tightly bound compounds (MBF3) mixed with $\text{Al}(\text{SO}_4)_3 \text{H}_2\text{O}$ and/or $\text{Fe}_2(\text{SO}_4)_3$ and with the high ionic exchange compounds starch, chitosan and lignin. When N and P are released from the chemicals containing these nutrients the matrix based fertilizers likely bind N and P to a $\text{Al}(\text{SO}_4)_3 \text{H}_2\text{O}$ and/or $\text{Fe}_2(\text{SO}_4)_3$ starch- chitosan- lignin matrix. After the starch-chitosan- lignin matrix with $\text{Al}(\text{SO}_4)_3 \text{H}_2\text{O}$ and/or $\text{Fe}_2(\text{SO}_4)_3$ is applied to soil the soil microorganisms degrade the starch in the matrix comparatively rapidly and create some ionic exchange sites. Chitosan degrades less rapidly than starch but more rapidly than lignin and retains most of its ionic exchange sites for as much as a year in soil environments. The lignin component in the matrix will degrade more slowly than starch and chitosan and is expected to retain its ionic exchange sites for several years in most soil environments. Nutrient availability and leaching can be controlled by varying the relative amounts of starch-chitosan-lignin matrix with $\text{Al}(\text{SO}_4)_3 \text{H}_2\text{O}$ and/or $\text{Fe}_2(\text{SO}_4)_3$ in the mixture. The MBFs bind nutrients to the $\text{Al}(\text{SO}_4)_3 \text{H}_2\text{O}$ and/or $\text{Fe}_2(\text{SO}_4)_3$ starch- chitosan- lignin matrix. Application rates must be calibrated to the amount of nutrients released to meet plant growth requirements. Therefore, their application rates will not be identical to conventional or slow release fertilizers. Subsequent experiments have shown comparable plant response among SRF and MBF formulations, while still reducing nutrient leaching via MBFs.

Mycorrhizal colonization in plant roots did not differ among SRF, MBF1, MBF2 and MBF3 formulations with or without $\text{Al}(\text{SO}_4)_3 \text{H}_2\text{O}$ and/or $\text{Fe}_2(\text{SO}_4)_3$. Mycorrhizal colonization was assessed at the termination of the experiment when roots were growing throughout the soil. The mycorrhizal associations with *G. interadicius* probably formed in the first few weeks of the experiment and subsequently, as roots grew and suberized, the colonizations at that location in the root diminished. *Glomus interadicius* is an arbuscular mycorrhizal fungi species that will form associations with a broad range of host plants in soils containing high concentrations of nitrogen and phosphorus. *Glomus interadicius* was added to the matrix to enhance plant uptake of N and P.

The impact of MBF fertilizers to reduce N and P leaching in the field may not be immediately apparent in agricultural soils with histories of heavy fertilization, especially P. Long histories of heavy fertilizer application results in nutrients being bound to or held on clay and organic matter ionic exchange sites (D' Angelo, 2005; McDowell et al., 2005; Bird et al., 2002; 2003; Devere and Horwath, 2001). Fertilizer N and P will also have become incorporated into organic matter complexes which will result in these nutrients being released as organic matter is decomposed (Bird et al., 2002; 2003 Entry and Emmingham, 1995) . The efficacy of MBF fertilizers to reduce N and P input to surface and ground water can be expected to be most effective on highly leached sandy soils rather than soils containing high concentrations of silt, clay or organic matter.

5.0 Conclusions

These new fertilizer formulations do not depend on organic or inorganic coatings to reduce N and P leaching and with further testing and development could conceivably be more effective at reducing nutrient leaching than current commercial slow release fertilizers. Although further greenhouse and field testing are called for, results of this initial investigation verify the effectiveness of the concept to reduce nutrient leaching. Preliminary results of subsequent research indicate that rate and formulation adjustments can meet plant nutrient and growth needs while still reducing leaching losses of nutrients. Cost of these MBF fertilizers has been calculated to be \$ 0.03-0.08 kg^{-1} above the cost of conventional fertilizers. One of the main

goals of future research should be to reduce the cost of MBF production. MBFs initially may be economically feasible for use by homeowner on their lawns, turf grass operators such as golf course managers and growers of high value agricultural crops. The MBF formulations could prove important in soils whose water flow drains into nutrient-affected waters such as the Chesapeake Bay, Florida Everglades and rivers flowing into the Great Lakes.

As nutrients are applied to a soil they can accumulate to the maximum retention capacity of the soil, which is controlled by soil physical and chemical properties, the resident biota and the rate of nutrient uptake by vegetation. Excessive application of any fertilizer eventually will load soil beyond its maximum retention capacity. Nutrients added to the soil above that limit via any mode of application are eventually released to water flowing over and/or through the soil. Improved technology can not substitute fully for adhering to sound land management practices. In the long term N and P contamination of water can be prevented only by applying nutrients in quantities relative to the inherent capacity of the soil to retain nutrients and the quantities removed via harvest. However, new MBF formulations that release nutrients at a rate comparable to plant uptake can reduce nutrient leaching and ultimately eutrophication.

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